California Environmental Protection Agency
AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Protocol for the Ambient Air Monitoring of Methomyl and Carbaryl

July 20, 2007

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The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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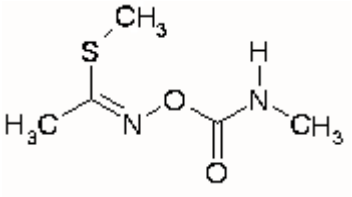
1.0 Introduction

At the request of the Department of Pesticide Regulation (DPR) (January 29, 2007 Memorandum, Warmerdam to Witherspoon), the Air Resources Board (ARB) will conduct ambient air monitoring for the pesticides methomyl and carbaryl in Fresno, Kings and Tulare Counties. Ambient Air monitoring for these two pesticides will occur over a period of six weeks. This monitoring was performed under the requirements of the California Code of Regulation, Food and Agriculture Code, Section 14022(c) which requires the ARB, "…to document the level of airborne emissions…of pesticides that may be determined to pose a present or potential hazard...", when requested by the DPR. Monitoring is being conducted to coincide with the use of methomyl as a selective pesticide on alfalfa and corn for human consumption.

The draft "Standard Operating Procedure Sampling and Analysis of S-methyl-N((methylcarbamoyl)oxy)thioacetamidate (Methomyl)" dated June 2007, is included as Appendix A.

2.0 Chemical Properties of Methomyl

Figure 1. Chemical structure of methomyl.



The following information on the physical/chemical properties of Methomyl (Chemical name: S-methyl-N((methylcarbamoyl)oxy)thioacetimidate; Molecular structure: $C_5H_{10}N_2O_2S$) (Figure 1) is a white crystalline solid with a slightly sulfurous odor with a solubility of 5.8 g/100 g water (DuPont 2005). It is stable under normal temperatures when dry, but thermal decomposition and combustion will produce hazardous gases including sulfur oxides, methyl isocyanate and hydrogen cyanide. Table 1 lists the physical and chemical properties of methomyl as obtained from DPR's, "Use Information and Air Monitoring, and Ambient Air Monitoring Recommendations for the Pesticide Active Ingredient Methomyl", dated June 2007 is included as Appendix B.

Chemical name	methomyl
Trade names†	Lannate
CAS Registry number	16752-77-5
Molecular formula	$C_5H_{10}N_2O_2S$
Molecular Weight	162.2 g/mol
Melting Point	78 – 79 ºC
Vapor Pressure	5.4 x 10^{-6} mmHg (25 °C)
Specific Gravity	1.2946 (24 ºC)
Water Solubility	58,000 mg/L (25 °C)
Henry's Law Constant	1.90 x 10^{-10} atm-m^3/mol (25 °C)
Soil Adsorption Coefficient (K_{oc})	43.3 cm^3/g
Field Dissipation Half-life	54 days, sandy loam soil
Octanol / Water Partition Coefficient (K_{ow})	0.60
Hydrolysis half life	30 days

Table 1.
Physical and chemical properties of methomyl (Hazardous Substances Data Bank. 2007; Crop Protection Handbook, 2007).

E.I. Du Pont De Nemours & Co. (Du Pont) currently registers two products containing methomyl — Lannate SP (soluble powder) and Lannate LV (liquid concentrate). Lannate SP contains a higher percentage of methomyl than Lannate LV (90% versus 29%) and accounts for the majority of agricultural use of methomyl in California. These products are applied directly to soil either by aerial application or ground spraying and are used as pesticides to control a wide range of insects including thrips, bugs, aphids, beetles, moths, diptera and ant-hymenoptera on a variety of commodities. (DPR Product/Label Database http://www.cdpr.ca.gov/docs/label). They are restricted use pesticides.

Methomyl is an n-methyl carbamate insecticide with anticholinesterase activity and as such carries a Poison/Danger signal word on the label. It is fatal if swallowed and may be fatal if inhaled. According to the label Lannate SP, the more widely used of the formulations, is a dry powder to be dissolved in water for application by mechanical ground or air equipment only. Hand-held equipment is prohibited for applications to crops and the pesticide must not be applied through any type of irrigation system. It should not be applied by ground equipment within 25 feet, or by air within 100 feet of lakes, reservoirs, rivers, estuaries, commercial fish ponds, natural streams, marshes or natural ponds.

† Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

3.0 Project Goals and Objectives

The goal of this monitoring project is to measure the concentrations of both methomyl and carbaryl in ambient air throughout the San Joaquin Valley counties of Fresno, Kings and Tulare.

To achieve the project goals, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.

2. Appropriate application of sampling/monitoring equipment to determine ambient methomyl and carbaryl concentrations.

3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.

4. At the conclusion of the project, MLD will provide DPR with a final report containing all relevant information, data and execution of this project.

4.0 Contacts

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5.0 Study Location and Design

Methomyl applications are performed throughout the San Joaquin Valley. DPR has identified that June, July, and August are when applications are at their peak.

Ambient Air Monitoring

Samples will be collected by passing a measured volume of ambient air through two XAD-2 resin tubes that are mounted on a sampling tree as shown in Figure 2. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (on dry ice) or in a freezer until extracted in the laboratory with organic solvent. The sampling flow rates of 2.0 liters per minute (LPM) for methomyl and carbaryl will be accurately measured and the sampling system operated continuously for 24 hours with the exact operating interval recorded in the logbook. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods and 1.5 meters above roofline or in an open secured area which meets siting criteria, for the ambient monitoring. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately. During the ambient air monitoring, one tube is used to collect methomyl and carbaryl simultaneously.

A rotameter is used to control sample flow rate and therefore two rotameters will be located on a collocated sampling tree. The first rotameter is used to control flow through the primary sample. The second rotameter is used to control flow through the collocated sample (four (4) collocated samples will be collected at each sampling location). The rotameters will have a scale from 0-5. The flow rates are set at 2.0 LPM, as measured using a digital mass flow meter (MFM) before the start of each sampling period. The flow rate will be checked with the MFM at the beginning and the end of each sampling period. Samplers will be leak checked prior to each sampling period with the sampling tubes installed. Any change in the flow rates will be recorded in the field logbook. The field logbook will also be used to record start and stop times, start and stop flow rates, start and stop counter readings, sample identifications and any other significant data.

The use maps for methomyl suggest that ambient monitoring should occur in Fresno, Kings and Tulare Counties during the months of June through August. Six sampling sites (five air monitoring sites and one urban background site) should be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). In addition to the primary samples, replicate (co-located) samples are needed for four dates at each sampling

location. The ambient air monitoring sites should be located in areas where there is high use of methomyl and where environmental justice factors are highest. Methomyl use in 2004-2005 and community environmental justice factors indicate that ambient air monitoring should occur over a 12-week period during June, July and August in the San Joaquin Valley region.

The ambient monitoring sites in the Fresno County communities are located at:

Huron Middle School
16875 Fourth St.
Huron, CA. 93234
(559) 945-8482 FAX (559) 945-8482

Mendota School Bus Barn
1993 Belmont
Mendota, CA. 93640
(559) 655-3433 FAX (559) 655-4299

Parlier Junior High School
1200 East Parlier Ave.
Parlier, CA. 93648
(559) 646-1660 FAX (559) 646-1633

The urban background site is located at:
The Air Resources Board's Air Monitoring Station
3425 N. First St.
Fresno, CA. 93726
(559) 228-1825 FAX (559) 228-0116

The ambient monitoring site in the Tulare County community is located at:
Richgrove School
20908 Grove Drive
Richgrove, CA. 93261
(661) 725-2427 FAX (661) 725-5772

The ambient monitoring site in the Kings County community is located at:
Kettleman City High School
707 General Petroleum Ave
Kettleman City, CA. 93239
(559) 386-9081 FAX (559) 386-0207

At each sampling site, four 24-hour samples will be collected per week during the sampling period. ARB personnel will collect the samples over a six-week period from July through August, 2007. The 24-hour samples will be taken Monday through Friday (4 samples/week) at a nominal flow rate of 2.0 LPM.

6.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) personnel will hand-carry samples to and from MLD's laboratory in Sacramento, and to and from the sampling location. The samples will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample.

At each sampling site, the operator will assure that at the end of each sampling period, the XAD-2 resin tube will be placed in culture tubes with an identification label affixed with a record of the run information on the field sample report. After collection the samples are place in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory. The sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. These samples will be stored in the freezer or extracted/analyzed immediately. Samples are collected in the field with a flow rate of two (2) liters per minute (LPM).

All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply SPM with XAD-2 resin tubes. NLB will perform analyses for both methomyl and carbaryl on collected ambient samples and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure Sampling and Analysis of S-methyl-((methylcarbamoyl)oxy)thioacetamidate (Methomyl). The SOP is included in this Protocol as Appendix A.

The following XAD-2 resin tube validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time**: Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established holding time will be invalidated by the Laboratory.

2. **Duplicate Analysis**: Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.

3. **Method Detection Limit (MDL)**: MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.

4. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

7.0 List of Field Equipment

Quantity	Item Description
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Alborg mass flow meter 0-5 LPM.
(1)	Dry ice chest
(1)	Ladder
(6)	Extension cords
(6)	Elapse time meters

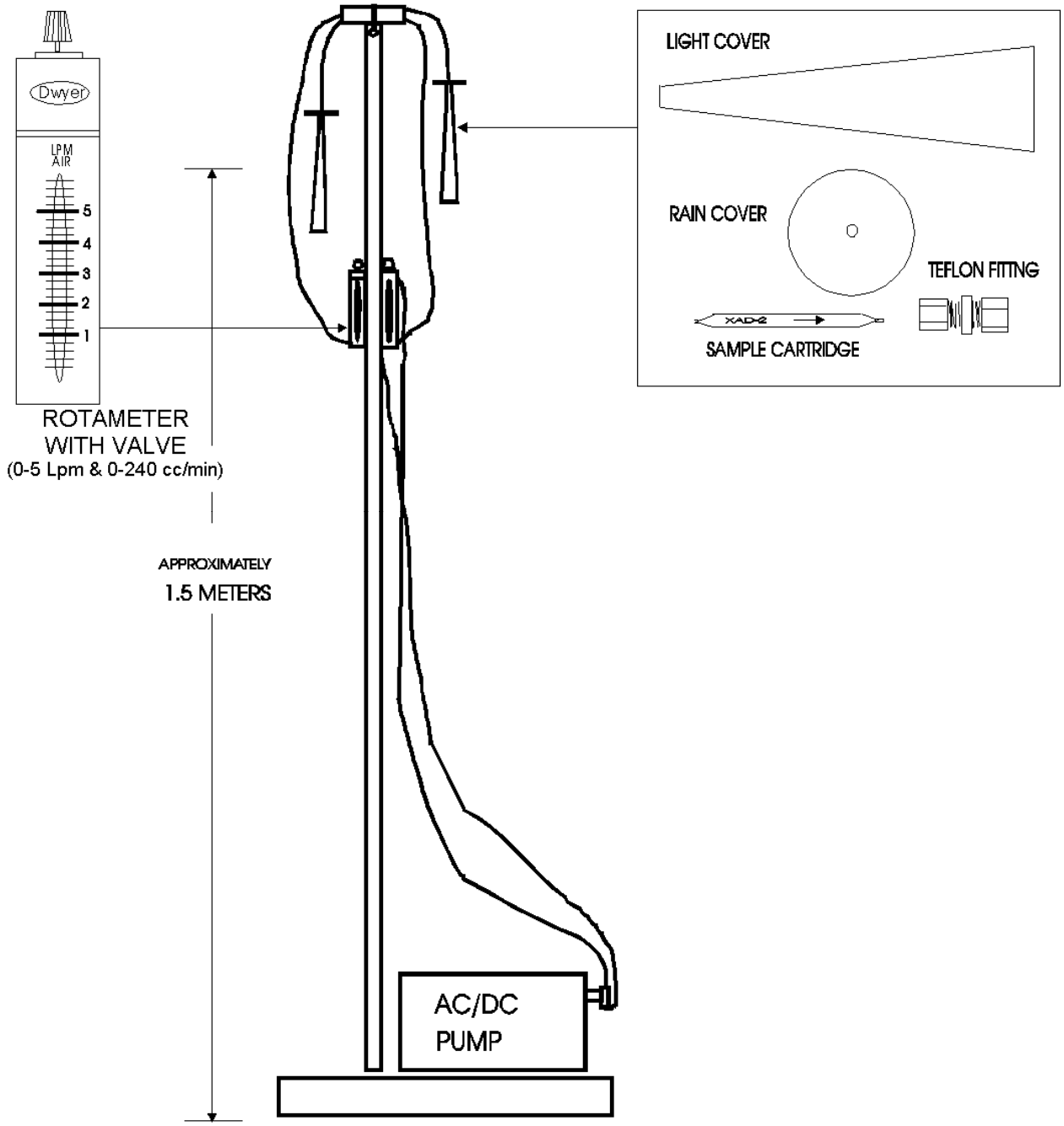

Figure 1
Air Sampler Tree with Pump

8.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the passive flow controllers will be measured using mass flow meters having a current calibration certification and a range of 0-5 liters per minute (LPM).

The metrological sensors will be calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link.

http://www.arb.ca.gov/aqdas/amwmn.php?c=5&t=sop

Each XAD-2 resin tube will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

Field Spike (FS): A field spike will be prepared by the laboratory by injecting a XAD-2 resin tube with 51 nanograms (ng) of methomyl. The field spike is installed onto a sampler and will be collocated next to the background sampler. The ambient field spikes will be co-located at the background site.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a XAD-2 resin tube at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler.

Trip Blank (TB): A trip blank will be prepared by the laboratory. The trip blank canister accompanies the sample canisters from the lab to the field and returns but is not installed onto a sampler.

Collocated (CO): For ambient monitoring, collocated (side-by-side) air samplers will operate at each site, on four (4) separate days, throughout the monitoring period.

Site/Sample Identification

The methomyl/carbaryl sampling sites will be named accordingly for the locations, Date and type of sample:

Ambient Site Naming:

FRE 1-24 Fresno ARB site Weeks 1 through 6
HUR 1-24 Huron site weeks 1 through 6
MEN 1-24 Mendota site Weeks 1 through 6
PAR 1-24 Parlier site Weeks 1 through 6
RIC 1-24 Richgrove site Weeks 1 through 6
KET 1-24 Kettleman City site Weeks 1 through 6

Letter Abbreviations as follows

FS = Field Spike
CO= Co-located
TS = Trip Spike
TB = Trip Blank

Following the quality control procedures listed above will insure the quality and integrity of the samples collected in the field and will insure accurate field and lab data collection.

9.0 Deliverables

9.1 Air Quality Surveillance Branch Deliverables

Within 60 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

1) Sampling Protocol.
2) Personnel Contact List.
3) Site Maps.
4) Site Photographs.
5) Site Descriptions and Measurements, GPS coordinates, inlet height.
6) A map of the monitoring site locations.
7) Sample Summary Table.
8 Field Sample Log.
9) Laboratory Analysis Reports with calculations in electronic format.
10) Met Station and Sampler Calibration Reports.
11) Transfer Standards' Certification Reports.
12) Disk containing electronic files of Report.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

9.2 Northern Laboratory Branch (NLB) Deliverables

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

1) Table(s) of sample to include:

    a. Sample identification (name).
    b. Date sample received from field.
    c. Date sample analyzed.
    d. Dilution ratio.
    e. Analytical results.

2) All equations used in calculating analytical results.

3) Table of duplicate results including calculated relative percent difference (RPD).

4) Table of collocated results.

5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries.

6) Table of analytical results from all trip blanks.

7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.

8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.

9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

Sample Log Sheet for Methomyl/Carbaryl Application and Ambient Air Monitoring								
Log- #	**Sample ID**	**Start Date/Time**	**End Date/Time**	**Sample Flow (Start)**	**Sample Flow (Stop)**	**ETM Start**	**ETM Stop**	**Comments**

Figure 2

Sample Field Log Sheet

APPENDIX A: Standard Operating Procedure Analyses for Methomyl

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for methomyl collected by the XAD-2 resin tube method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of S-methyl-((methylcarbamoyl)oxy)thioacetamidate (Methomyl).

California Environmental Protection Agency

Air Resources Board

DRAFT

Standard Operating Procedure
Sampling and Analysis of S-methyl-N((methylcarbamoyl)oxy)thioacetamidate (Methomyl) and 1-naphthalenylmethylcarbamate (Carbaryl)

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

August 2007

Version 1

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

This is a high pressure liquid chromatography/mass spectrometer (LC/MS) method for the determination of S-methyl-N((methylcarbamoyl)oxy)thioacetamidate (Methomyl) and 1-naphthalenylmethylcarbamate (Carbaryl) from ambient air samples.

2. SUMMARY OF METHOD

Ambient air samples are collected on XAD-2 cartridges. Sampled cartridges are stored at 4 degrees centigrade (°C) or lower prior to extraction. Sample extraction is a two step process involving an initial extraction to remove the Methomyl followed by the addition of more ACN to facilitate the extraction of Carbaryl. Two separate instrument methods are use to analyze for Methomyl and Carbaryl. Sample analysis is performed using a high performance liquid chromatograph with a mass spectrometer (LC/MS) in the selected ion-monitoring mode (SIM). Sample analysis and quantitation uses an external standard method for instrument calibration. Estimated quantitation level for this method is approximately 0.001 and 0.032 microgram per cubic meter ($\mu g/m^3$) for methomyl and carbaryl respectively, prior to any sample dilution.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 cartridges that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. Both a system blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Agilent Instruments 1100 Series liquid chromatograph with LC/MSD SL analyzer (or equivalent):

Binary Pump Parameters:

Column Flow 1.0 ml/min
Stop Time 15.0 minutes
Post Time 5.0 minutes
Solvent Gradient: Methomyl
25% ACN/75% H2O at 0.0 minutes
60% ACN/40% H2O at 10.0 minutes
80% ACN/20% H2O at 14.0 minutes

Solvent Gradient: Carbaryl

45% ACN/55% H2O at 0.0 minutes
60% ACN/40% H2O at 10.0 minutes
80% ACN/20% H2O at 12.0 minutes

Column:
Allure C18 5um 150 x 4.6 mm (or equivalent)
Oven Temperature at 35 º C

Agilent LC/MSD SL Detector with Multimode Ionizer (or equivalent)
Ionization mode: MM-APCI
Polarity: Positive
Spray Chamber:
Gas (nitrogen) temperature: 350 º C
Vaporizer temperature: 250 º C
Drying Gas: 8 liters/minute
Nebulizer Pressure: 20 psig
Capillary Voltage: 2000 volts
Corona Current: 5.0 µA
Charging Voltage: 2000 volts

Acquisition Mode: SIM
Masses: 88.1, 145.1, 163.1, 202.1,
Fragmentor: 60, 140
Gain: 4.0
Dwell Time: 319 milliseconds

Tune File: APCI autotune

B. Auxiliary Apparatus

XAD-2 cartridges (400/200 mg) (SKC cat # 226-30-6) or equivalent
Glass amber vials, 2-ml capacity with septum caps.
Sonicator

C. Reagents

Acetonitrile (B&J brand HPLC grade or equivalent)
Water Millipore 18 mohm –cm or equivalent
Methomyl 98.5% pure (Chem Service Inc. PS-1020)
Carbaryl 99.5% pure (Chem Service Inc. PS-84)

D. Gases

Liquid Nitrogen at 350 psig or N_2 generator yielding 99% pure N_2 at 90 psig

5. SAMPLE COLLECTION

a) Samples are collected in the field with a maximum flow rate of two (2) liters per minute (lpm).
b) After collection the samples are place in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory.
c) Methomyl and to a lesser extent Carbaryl is stable for up to 28 days when kept at -20°C. See section F for the storage stability summary.

6. SAMPLE EXTRACTON

a) Prepare a method blank and laboratory control sample (LCS) cartridge with every batch of field samples not to exceed twenty (20) samples in an analytical batch.
b) Spike the LCS with approximately 50 ng of methomyl and 700 ng of Carbaryl before extraction.
c) Carefully score and break the XAD-2 cartridge just above the glass wool plug on the primary section.
d) Remove the glass wool plug using forceps.
e) Pour the XAD-2 resin from the primary section into the glass vial.
f) Carefully score and break the XAD-2 cartridge just above the glass wool plug on the secondary section.
g) Carefully rinse the primary section glass segment with 2.0 ml of 50% ACN/H_2O into the 8 ml vial. Cap tightly.
h) Retain the secondary section for later analysis to check for breakthrough.
i) Place all the 8 ml vials in an ultrasonic bath and sonicate for 30 to 45 minutes.
j) At the end of the initial sonication add 1 ml of ACN to each vial. Recap and sonicate for an additional 30 to 45 minutes.
k) Place 8 ml vial with XAD-2 and extract into a refrigerator until analysis.

7. ANALYSIS OF SAMPLES

a) Just prior to analysis transfer approximately 0.5 ml of the sample extract to a 1.5-ml autosampler vial equipped with a 0.5 ml insert. Sample extract is now ready for analysis.
b) A 10 µl injection volume will be used for Carbaryl and a 40 µl injection volume for the Methomyl analyses.
c) Perform an initial calibration curve using concentrations at or near the EQL to approximately 100 times higher. At least 5 points must be

analyzed to establish a calibration curve. Appendix 1 lists the concentrations used.

d) Prepare a sample sequence for the LC/MSD. The sequence should include a system blank, and a calibration curve or a continuing calibration verification standard (CCV), for every 10 samples analyzed. If this batch of samples includes a method blank and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.

e) Because of the nature of the XAD-2 cartridge, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every 10 to 20 sample or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.

f) Review and edit the quantitation reports as needed.

g) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.

h) The final results will be adjusted by an appropriate dilution factor and reported in µg/sample.

i) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc } (\mu g/m^3) = \frac{\text{Extract Conc (ng/ml) x 3 ml}}{\text{Air Volume Sampled } (m^3) \text{ x } 1000}$$

k) Given instrument sensitivity and a maximum sample volume of 2.9 m^3 the EQLs for this method will be approximately 0.001 µg/m^3 for methomyl and 0.032 µg/m^3 for carbaryl.

8. QUALITY ASSURANCE

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. Tables 1 and 2 list the results for the methomyl and carbaryl instrument reproducibility study.

TABLE 1
INSTRUMENT REPRODUCIBILITY
METHOMYL (ng/ml)

Low Level	Medium Level	High Level	
4.07	18.9	86.3	
4.02	19.3	85.4	
4.09	18.6	86.2	
3.55	18.9	85.5	
3.90	18.9	87.2	
3.93	18.94	86.14	Average
0.2196	0.2385	0.7038	Std Dev
5.588	1.259	0.817	RSD

TABLE 2
INSTRUMENT REPRODUCIBILITY
CARBARYL (ng/ml)

Low Level	Medium Level	High Level	
82.36	339.64	1531.47	
80.35	323.68	1349.92	
83.17	319.50	1422.17	
86.56	324.41	1364.04	
80.93	318.27	1441.37	
82.77	325.10	1421.79	Average
2.3326	8.5427	72.3076	Std Dev
0.02818	0.02628	0.05086	RSD

B. Linearity

A 5 or 6-point calibration is performed. Calibration standards ranging from at or near the EQL to approximately 100 times higher are used for methomyl and carbaryl. The results are used to calculate calibration curves using linear or quadratic regression. An r^2 of 0.995 or higher is required for an initial calibration to be acceptable. A CCV will be run at the start of each analytical batch, and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25% of the actual value.

C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicates of a low-level standard, the MDL and EQL for Methomyl and Carbaryl are calculated as follows:

$$MDL = 3.143*STD$$

$$EQL = 5*MDL$$

STD equals the standard deviation of the calculated results for the seven replicate spikes. The calculated MDLs for methomyl/carbaryl are 0.2738/6.439 ng/m^3 based on a 2.9 m^3 sample collection volume and a 3 ml extraction volume. The EQL for methomyl/carbaryl using a three-ml extraction volume and a sample collection volume of 2.9 m^3 is 1.369/32.197 ng/m^3.

D. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The LCS stock standard should come from a different source or lot then the daily calibration standards. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed.

E. Collection and Extraction Efficiency (Recovery)

Collection and efficiency (recovery) data for Methomyl and Carbaryl should be established prior to sample analysis. Using two concentration levels (51 and 570 ng) the recovery for methomyl was as follows: An average recovery of 44ng with a standard deviation of 1.32 was achieved for the low level spikes, while an average recovery of 532 ng with a standard deviation of 12.53 was achieved for the high level spikes. Carbaryl was spiked at 300ng and 3600 ng. The recovery for carbaryl was as follows: An average recovery of 270 ng with a standard deviation of 5.89 was achieved for the low level spike, while an average recovery of 3720 ng with a standard deviation of 10.6 was achieved for the high level spike.

F. Storage Stability

Storage stability studies were performed in triplicate using 52 ng methomyl spiked on the primary section of XAD-2 cartridges. The project was run for 28 days with cartridges being tested at 0, 7, 14, 21, 28 days. Tables 3 and 4 list the results for the storage stability study.

Table 3
Storage Stability Study
Methomyl 2007

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Dev
0	107.12	97.41	96.59	100.37	5.86
7	99.88	98.53	100.76	99.73	1.13
14	89.41	84.41	83.47	85.76	3.19
21	91.71	94.24	95.06	93.67	1.75
28	87.94	89.06	89.12	88.71	0.66

Table 4
Storage Stability Study
Carbaryl 2007

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Dev
0	79.34	78.71	72.30	76.79	3.90
7	74.30	80.53	74.63	76.49	3.50
14	56.40	70.30	58.16	61.62	7.57
21	48.12	63.58	70.27	60.65	11.36
28	69.14	61.00	71.20	67.11	5.39

G. Breakthrough

Methomyl breakthrough was evaluated at three concentrations, 51 ng, 570 ng, and 5000 ng. Three XAD-2 cartridges were spiked at each concentration level. Air was collected at approximately two liters per minute for 24 hours. Methomyl was not detected in the back section of the XAD-2 cartridges. Average recovery for methomyl from the front sections was 83, 93 and 78 per cent, respectively. Carbaryl breakthrough was evaluated at 300 and 3600 ng. As with methomyl air was collected at

two liters per minute for 24 hours. No carbaryl was detected in the back section of the XAD-2 cartridges. Average recovery for carbaryl was 90 and 103 per cent respectively.

H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Appendix 1

Calibration Standard Preparation for Methomyl and Carbaryl

The certified neat standard used for calibration was purchased from Chem Service Inc., West Chester, Pennsylvania and has the following specification:

Lot No:	344-83A
Expiration date:	July 2011
Methomyl:	98.5% pure (solid)
Carbaryl:	99.5% pure (solid)

A stock standard with a concentration of approximately 1-milligram (mg) per ml was prepared by weighing 25 mg of methomyl and 25 mg of Carbaryl into a 25 ml volumetric flask and bringing to volume with methanol.

Using a serial dilution technique the following calibration standards were prepared in acetonitrile: 1.0, 5.0, 10.0, 20.0, 50.0, and 100.0 ng/ml for methomyl and 16, 80, 150, 320, 700, 1450 ng/ml for carbaryl.

The calibration curve was generated using six standard concentrations, with the Methomyl and Carbaryl standard at 1.0/16 ng/ml being the low point. The low point equates to approximately 0.345/5.52 ng/m^3 respectively.

All standard and sample injections used a volume of 40 µl for methomyl and 10 µl for carbaryl

Initial calibration curve acceptance requires an r^2 of at least 0.995.

APPENDIX B:

USE INFORMATION AND APPLICATION MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT METHOMYL AND THE AMBIENT AIR MONITORING RECOMMENDATIONS FOR METHOMYL AND CARBARYL

HTTP://WWW.CDPR.CA.GOV/DOCS/EMON/PUBS/TAC/RECOMM/METHOMYL_FINAL.PDF